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Pulling a polymer at an interface: directed walk models

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Abstract

We consider directed walk models of a homopolymer (in two dimensions) interacting with two immiscible liquids. The polymer is subject to a force, normal to the interface between the two liquid phases. We first consider the case where, in the absence of a force, the polymer is delocalized into the preferred bulk phase, but is pulled into the less favourable bulk phase by the applied force. We examine the temperature dependence of the critical force as a function of the relative quality of the two solvents. When both solvents are poor the polymer can localize at the interface and we also consider the temperature dependence of the critical force needed to pull the polymer out of the interface and into a bulk phase.

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1. Introduction

The availability of experimental methods for micromanipulation of polymer molecules has led to an interest in developing theories of the unzipping of duplex DNA molecules by an applied force (Marenduzzo *et al* 2001, 2002). The temperature dependence of the critical force for unzipping shows interesting features and, in particular, the phase diagram in the force–temperature plane can show re-entrant behaviour. The re-entrant behaviour has been seen both in a self-avoiding walk model (Orlandini *et al* 2001) and in a directed walk model (Marenduzzo *et al* 2001). Micromanipulation techniques can also be used to study the effect of an applied force on the adsorption of linear polymers at a surface or on the localization of polymers at an interface between two immiscible liquids (Chatellier *et al* 1998, Bemis *et al* 1999).

Polymer adsorption and localization in the absence of an applied force have been widely studied for many different models of the configurational properties of the polymer. Directed walk models of adsorption of homopolymers are rather well understood (Privman *et al* 1988, Whittington 1998, Janse van Rensburg 2000, 2003) and give considerable insight into the

physics of the problem. In a similar way directed walk models have contributed to our understanding of the phenomenon of localization of a polymer at the interface between two immiscible liquids (Bolthausen and den Hollander 1997, Biskup and den Hollander 1999, Orlandini *et al* 2002).

In this paper we consider directed walk models of a homopolymer and a pair of immiscible liquids with a planar interface. We restrict our attention to the case where the first monomer of the polymer is in the interface between the two liquids. If the polymer is soluble in one liquid and insoluble in the other it will be delocalized into one liquid phase. We then apply a tensile force to the last monomer, in a direction perpendicular to the interface, so as to pull the polymer from the preferred liquid phase to the other phase. We ask for the temperature dependence of the critical value of the force needed to move the polymer from one phase to the other. We also consider the situation in which the polymer sits at the interface (i.e. it is localized) and apply a force to pull it into one of the liquid phases. Again we ask for the temperature dependence of the critical value of the force.

2. A model related to Dyck paths

The model which we shall consider in this section is a directed walk model in two dimensions related to bilateral Dyck paths. Consider walks on the vertex set of the square lattice (having coordinate system (x_1, x_2)) with edges of length $\sqrt{2}$ in directions $(1, 1)$ and $(1, -1)$. A *Dyck path* is a walk with edges of these two types, starting at the origin, having no vertex with negative x_2 -coordinate and with the last vertex in the line $x_2 = 0$. A *bilateral Dyck path* has the same types of edges, starts at the origin and has its last vertex in $x_2 = 0$. That is it can cross the line $x_2 = 0$. We shall be concerned with walks with the same types of edges, which start at the origin and have their last vertex in the line $x_2 = h$. The case $h = 0$ corresponds to bilateral Dyck paths. A special case is a *tail* which is a walk which starts at the origin and has no other vertices in $x_2 = 0$.

Let $w_n(u, v, h)$ be the number of such walks with n edges, having u vertices with positive x_2 -coordinate, v vertices with negative x_2 -coordinate and with the last vertex in the line $x_2 = h$. Define the generating functions

$$W(a, b, y, z) = \sum_{u,v,h,n} w_n(u, v, h) a^u b^v y^h z^n \quad (2.1)$$

and

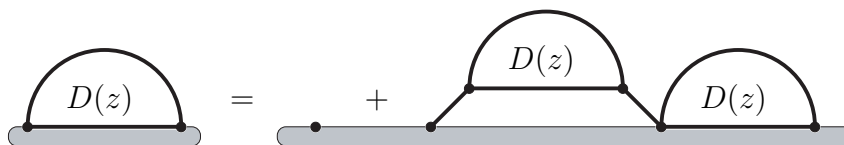
$$W^+(a, b, y, z) = \sum_{u,v} \sum_{h \geq 0} \sum_n w_n(u, v, h) a^u b^v y^h z^n. \quad (2.2)$$

We shall call the positive half-space $x_2 > 0$ the α -phase and the negative half-space $x_2 < 0$ the β -phase.

We now show how $W^+(a, b, y, z)$ can be calculated in terms of the generating functions of Dyck paths, bilateral Dyck paths and tails. Let d_n be the number of Dyck paths with n edges. By convention we set $d_0 = 1$. Define the generating function

$$D(z) = \sum_n d_n z^n. \quad (2.3)$$

Dyck paths can be factored according to the following scheme,



so that $D(z)$ satisfies the recurrence relation

$$D(z) = 1 + z^2 D(z)^2 \tag{2.4}$$

from which we obtain

$$D(z) = \frac{1 - \sqrt{1 - 4z^2}}{2z^2}. \tag{2.5}$$

Let the generating function for bilateral Dyck paths be $B(a, b, z)$, with a conjugate to the number of vertices in the positive half-plane, b conjugate to the number of vertices in the negative half-plane and z conjugate to the number of edges. Every bilateral Dyck path is either

1. a single vertex, which contributes unity to $B(a, b, z)$, or
2. a Dyck path with all except its first and last vertices having $x_2 > 0$, possibly followed by a bilateral Dyck path, or
3. a Dyck path with all except its first and last vertices having $x_2 < 0$, possibly followed by a bilateral Dyck path.

Factoring every bilateral Dyck path (except the single vertex) at the first return to the line $x_2 = 0$ gives

$$B(a, b, z) = 1 + z^2 [aD(az) + bD(bz)]B(a, b, z) \tag{2.6}$$

so that

$$B(a, b, z) = \frac{1}{1 - z^2 [aD(az) + bD(bz)]}. \tag{2.7}$$

B has two square root singularities

$$z_1 = \frac{1}{2a} \quad z_2 = \frac{1}{2b} \tag{2.8}$$

and a third singularity corresponding to a zero of the denominator of B , i.e.

$$z_3 = \frac{\sqrt{(a+b-ab)(a-1)(b-1)}}{a+b-2ab}. \tag{2.9}$$

Note that z_3 only occurs in the region of the (a, b) -plane where $b < a/(2a - 1)$.

Let $H(a, y, z)$ count walks starting at the origin, with no vertices having x_2 -coordinate negative, where a is conjugate to the number of vertices in the positive half-plane, y is conjugate to the x_2 -coordinate of the last vertex and z is conjugate to the number of edges. Let $T^+(y, z)$ be the generating function of tails where y is conjugate to the x_2 -coordinate of the last vertex, $x_2 > 0$ so only positive powers of y appear, and z is conjugate to the number of edges. These are related by

$$T^+(y, z) = yzH(1, y, z). \tag{2.10}$$

Walks contributing to $H(1, y, z)$ are either Dyck paths or Dyck paths followed by a tail so we have the relation

$$H(1, y, z) = D(z) + D(z)T^+(y, z). \tag{2.11}$$

Combining (2.10) and (2.11) gives

$$H(1, y, z) = \frac{D(z)}{1 - yzD(z)}. \tag{2.12}$$

Note that for each tail in the positive half-space, all except the first vertex has positive x_2 -coordinate. Weighting such vertices with the factor a gives

$$T^+(y, az) = ayzH(1, y, az). \tag{2.13}$$

Now we are ready to calculate W^+ by another factorization argument. Walks contributing to W^+ are bilateral Dyck paths and bilateral Dyck paths followed by a tail in the positive half-space. Therefore

$$W^+(a, b, y, z) = B(a, b, z) + B(a, b, z)T^+(y, az). \quad (2.14)$$

The generating function W^+ has the same three singularities as those of B , i.e. z_1, z_2 and z_3 given in (2.8) and (2.9) and, in addition, a fourth singularity

$$z_4 = \frac{y}{a(1+y^2)} \quad (2.15)$$

which is associated with the tail contribution.

In the next two sections we explore how the singularity structure of W^+ can be used to predict the phase diagram for a directed walk with an applied force, both in the delocalized and in the localized regime.

3. The delocalized case

In this section we consider a polymer delocalized into the β -phase and we shall consider the case $b > a \geq 1$. We argue that it is sufficient to consider W^+ instead of W . Suppose that the walk is delocalized into β and the x_2 -coordinate of its last vertex is $h < 0$. For every finite $h < 0$ the free energy will be identical to the case $h = 0$, so we can restrict our attention to walks with $h \geq 0$, i.e. to walks counted in W^+ . There is no cost in free energy in pulling the last vertex into the plane $x_2 = 0$.

Since $b > a, z_2 < z_1$ which reflects the fact that in the absence of an applied force the walk is delocalized into the β -phase. When the force is applied ($y > 1$) the competing singularity is z_4 and the phase boundary in the (a, b, y) -space is determined by the solution to the equation $z_4 = z_2$, i.e. by

$$y = \frac{b + \sqrt{b^2 - a^2}}{a}. \quad (3.1)$$

To introduce temperature (T) and force (f) explicitly we make the substitutions

$$y = e^{f/T} \quad (3.2)$$

and

$$a = e^{-\epsilon_1/T} \quad b = e^{-\epsilon_2/T}. \quad (3.3)$$

Since the ratio ϵ_1/ϵ_2 characterizes the relative solvent quality of α and β , without loss of generality we can set $\epsilon_2 = -1$ and write $\epsilon_1 = -\epsilon$. We note that $b > a$ corresponds to $\epsilon < 1$ and that increasing values of ϵ correspond to increasing the quality of the α -solvent. When $\epsilon = 1$ the α and β -solvents are both equally good. Making these substitutions in (3.1) gives the temperature dependence of the critical force, $f_c(T, \epsilon)$, as a function of the relative solvent quality ϵ . The T -dependence of f_c at various values of ϵ is shown in figure 1. Note that $f_c(0, \epsilon) = 1 - \epsilon$ and that $f_c(T, \epsilon)$ increases with T at fixed ϵ and decreases with ϵ at fixed T . At any fixed $\epsilon < 1$ and $f = 0$ the walk is delocalized in the β -phase and has positive entropy. There is a loss of entropy when the walk is subjected to a force $f > 0$ and this entropy loss plays a larger role at higher temperatures. Hence $f_c(T, \epsilon)$ is an increasing function of T . Smaller values of ϵ correspond to the solvent α being increasingly poor compared to solvent β . Hence, as ϵ decreases, there is an increasingly important energetic disadvantage when the polymer is moved into the α -phase.

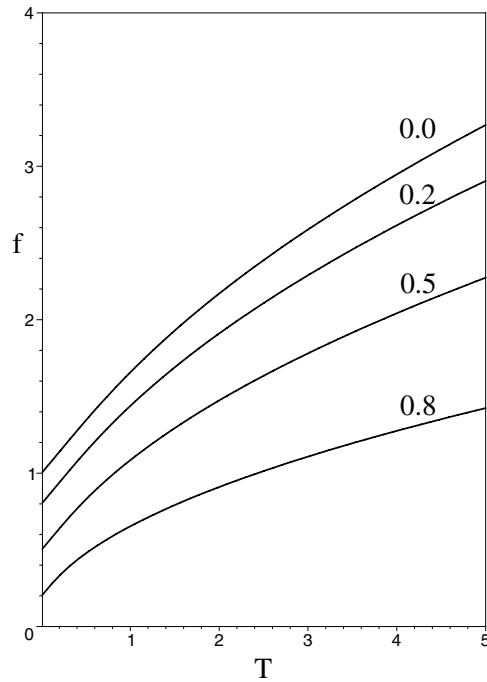


Figure 1. The temperature dependence of the critical force to pull a polymer from one bulk phase to the other. The curves are for $\epsilon = 0.0, 0.2, 0.5$ and 0.8 . At fixed T the force decreases as ϵ increases.

4. The localized case

When $a, b < 1$ the singularity z_3 exists and, in the absence of a force, leads to a localized phase (Orlandini *et al* 2002). One can think of the interfacial line as modelling a thin layer of a third liquid (immiscible with the other two liquids) in which the homopolymer is soluble. With $a, b < 1$ it is energetically favourable for the polymer to avoid the two bulk phases in favour of this third interfacial phase. (Note that there is no energetic disadvantage when a vertex is in the interfacial line $x_2 = 0$.) The phase boundary between the localized phase (controlled by z_3) and the phase in which the polymer is delocalized into the α -phase is given by

$$b = \frac{a(2a - 1)}{1 - 2a + 2a^2}. \tag{4.1}$$

This phase boundary passes through the points $(1, 1)$ and $(1/2, 0)$. When the polymer is being pulled into the α -phase the phase behaviour is controlled by the competition between the singularities z_3 and z_4 , so the phase boundary is the solution of the equation $z_3 = z_4$, i.e.

$$y = \frac{a + b - 2ab - a^2 + a^2b}{a\sqrt{(a + b - ab)(a - 1)(b - 1)}}. \tag{4.2}$$

In this case we make the substitutions

$$y = e^{f/T} \tag{4.3}$$

and

$$a = e^{-\epsilon/T} \quad b = e^{-1/T} \tag{4.4}$$

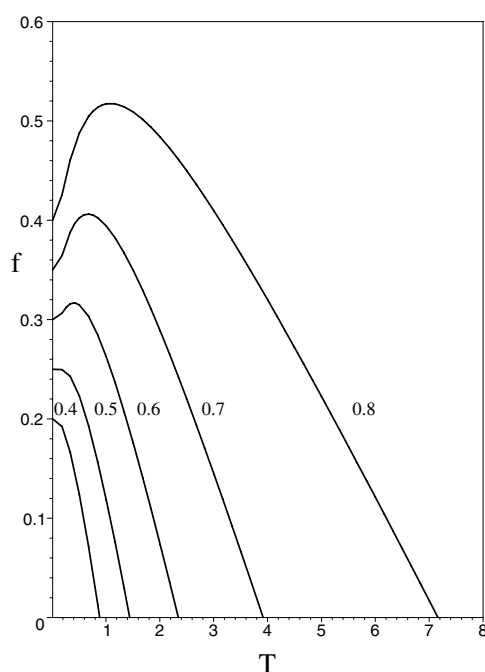


Figure 2. Temperature dependence of the critical force to pull a polymer from the interface to a bulk phase when the bulk phases are both unfavourable. As the two phases become more similar the force increases. The curves are for $\epsilon = 0.4, 0.5, 0.6, 0.7$ and 0.8 .

with $0 \leq \epsilon < 1$. Note the difference in the sign convention for ϵ used in this section and in the previous section. Larger positive values of ϵ now correspond to worse solvents. In figure 2 we show the temperature dependence of the critical force at various values of ϵ . These curves show several interesting features. For every T , $f_c(T, \epsilon)$ is monotone increasing in ϵ . When $\epsilon \leq 1/2$, $f_c(T, \epsilon)$ is a monotone decreasing function of T . When $\epsilon > 1/2$, $f_c(T, \epsilon)$ goes through a maximum as T increases and the location of the maximum increases as ϵ increases. That is, the phase diagram is reentrant for $1 > \epsilon > 1/2$. To investigate the low-temperature behaviour in more detail we show an enlargement of the figure near $T = 0$ in figure 3. We note that $f_c(0, \epsilon) = \epsilon/2$ and all the curves have zero slope at $T = 0$. When $\epsilon = 1$ the curve has positive slope at $T = 0$ and the force is monotone increasing in T . We return to this point in section 6.

In the absence of a force the phase transition is second order, i.e. the fraction of vertices in the interfacial line is a continuous but not differentiable function of the temperature. With any non-zero force the phase transition is first order.

5. A model related to Motzkin paths

Dyck paths have the disadvantage that they cannot lie entirely in the interface between the two bulk phases. We have therefore considered a somewhat more general model, related to Motzkin paths. The argument follows the idea used for Dyck paths in section 2 and we give only a sketch. A Motzkin path is a directed walk on the vertex set of the square lattice with the following restrictions:

1. the walk can have three kinds of edges, two of length $\sqrt{2}$ in directions $(1, \pm 1)$ and one of length 1 in direction $(1, 0)$,

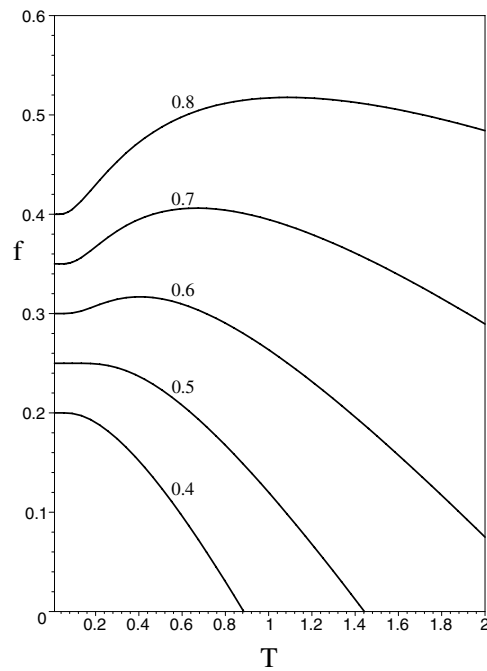


Figure 3. An enlargement of figure 2 to show the behaviour close to $T = 0$.

- 2. the walk starts at the origin and ends in the line $x_2 = 0$, and
- 3. the walk has no vertices with negative x_2 -coordinate.

Every Motzkin path begins with a set of edges (possibly empty) in $x_2 = 0$. The Motzkin path then leaves $x_2 = 0$. At its first return the Motzkin path is either complete or is completed by another Motzkin path. If $M(z)$ is the generating function of Motzkin paths then the initial edges in $x_2 = 0$ contribute $1 + z + z^2 + \dots = 1/(1 - z)$ to $M(z)$. Then factoring the path at its first return to $x_2 = 0$ shows that M satisfies the relation

$$M(z) = \frac{1}{1 - z} [1 + z^2 M(z)^2] \tag{5.1}$$

so that

$$M(z) = \frac{1 - z - \sqrt{1 - 2z - 3z^2}}{2z^2}. \tag{5.2}$$

Let $A(a, b, z)$ be the generating function for bilateral Motzkin paths (i.e. where condition (3), above, is relaxed), where a and b are conjugate to the numbers of vertices with $x_2 > 0$ and $x_2 < 0$, and z is conjugate to the number of edges. Since a bilateral Motzkin path is either a (possibly empty) set of edges in $x_2 = 0$, or a set of edges in $x_2 = 0$ followed by a Motzkin path either in the upper or in the lower half-space followed by a bilateral Motzkin path, another factorization argument shows that A satisfies the relation

$$A(a, b, z) = \frac{1}{1 - z} (1 + z^2 [aM(az) + bM(bz)]A(a, b, z)) \tag{5.3}$$

so that

$$A(a, b, z) = \frac{2ab}{2ab - a - b + a\sqrt{1 - 2bz - 3b^2z^2} + b\sqrt{1 - 2az - 3a^2z^2}}. \tag{5.4}$$

The generating function A has three physically relevant singularities,

$$z_1 = \frac{1}{3a} \quad z_2 = \frac{1}{3b} \quad (5.5)$$

and a singularity z_3 corresponding to a zero of the denominator of A . This third singularity only exists when $2ab - a - b \leq 0$, i.e. in the third quadrant of the $(\log a, \log b)$ plane.

The remainder of the argument leading to an expression for W^+ is almost identical to that given in section 2. For this model the generating function W^+ has four singularities, the three singularities of A discussed above and a fourth singularity

$$z_4 = \frac{y}{a(1 + y + y^2)} \quad (5.6)$$

which is associated with the tail contribution. Proceeding as in sections 3 and 4 we can derive the force–temperature diagrams corresponding to figures 1 and 2. The behaviour is very similar to the Dyck path case, although of course there are quantitative differences. For the localized case the phase diagram is again reentrant for $\epsilon > 1/2$ and the critical force has zero slope at $T = 0$ as in figures 2 and 3. However, when $\epsilon = 1$ the force is monotone increasing in T but still has zero slope at $T = 0$. As discussed in section 6, this is related to the unique ground state for this model.

6. Discussion

We have analysed directed walk models of the behaviour of a homopolymer in a system with two immiscible liquids when it is subject to a force. We considered two cases, where the polymer is delocalized into one phase and then pulled into the other, and where the polymer is localized at the interface and then pulled into one of the bulk phases. The force–temperature phase diagrams are very different in the two cases and, in the second, depend crucially on the relative quality of the two solvents. The localization–delocalization transition is second order in the absence of a force but is first order when a force is applied.

We first look at the case where the polymer is in one bulk phase and is then pulled into the other. The force is monotone increasing in the temperature and $f_c(0, \epsilon) = 1 - \epsilon$. We can understand the behaviour close to $T = 0$ by a simple approximate argument as follows. Consider a polymer with m monomers in the α -phase and $n - m$ in the β -phase. If we ignore the entropy of the polymer in the α -phase (because it is under tension), then the entropy contribution is $(n - m) \log \mu$, where $\mu = 2$ for the Dyck path model. The energy is $-mf - \epsilon m - (n - m)$ (since $\epsilon_2 = 1$). Hence the free energy is approximately given by

$$F = -mf - \epsilon m - (n - m) - T(n - m) \log 2 \quad (6.1)$$

and we differentiate with respect to m and set the derivative equal to zero, giving a critical value of f

$$f_c = 1 - \epsilon + T \log 2. \quad (6.2)$$

If $f > f_c$ the free energy is minimized by setting $m = n$ while if $f < f_c$ it is minimized by setting $m = 0$, so f_c is the critical force. At $T = 0$ we have $f_c(0, \epsilon) = 1 - \epsilon$, and (differentiating with respect to T) we see that the $f_c(T, \epsilon)$ has positive slope (equal to $\log 2$) at $T = 0$ for every $\epsilon \in [0, 1]$.

In the localized regime, close to $T = 0$ we expect the polymer to lie as close to the interface as possible. The details are different for the two models related to Dyck and Motzkin paths and we consider the Dyck path version. With $\epsilon < 1$ the energy is minimized by having half the vertices in α and half in the interface and we expect this to be the ground state. (This

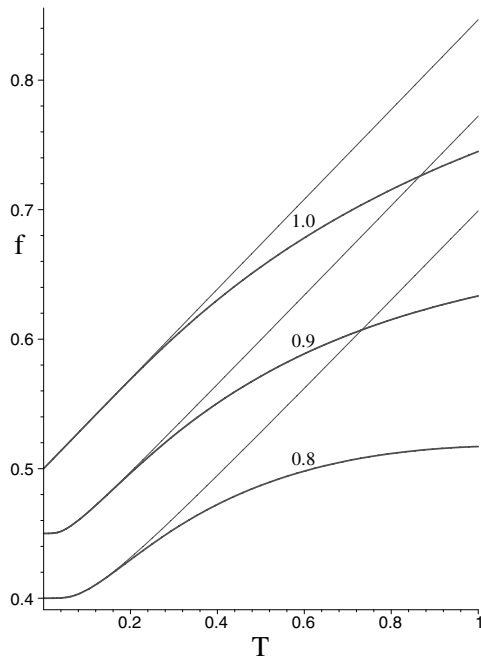


Figure 4. The temperature dependence of the critical force to pull a polymer from the interface into a bulk phase. The pairs of curves are for the exact force (for the Dyck path model) and for that derived from the approximate equation (6.5). The three sets of curves are for $\epsilon = 0.8, 0.9$ and 1.0 .

comes from the geometry of the walks.) Hence at temperature T with force f the free energy in this approximation (i.e. at very low temperature) is given by

$$F = -mf + m\epsilon + \frac{(n - m)}{2}\epsilon. \tag{6.3}$$

Following the above procedure we find that $f_c(0, \epsilon) = \epsilon/2$. When $\epsilon = 1$ the ground state will be degenerate since vertices not in the line $x_2 = 0$ can be in $x_2 = \pm 1$ and will have the same energy in either of these two lines. Hence at $T = 0$ there will be a residual entropy when $\epsilon = 1$. For $\epsilon < 1$ there will be a similar entropy contribution for $T > 0$ and this will be larger as ϵ approaches 1. In this case there is an energy penalty for having vertices in the β phase. When $\epsilon \leq 1$ we can estimate the free energy at small values of T by writing

$$\begin{aligned} F &= -mf + m\epsilon - T \log \sum_{l=0}^{(n-m)/2} \binom{(n-m)/2}{l} (e^{-1/T})^l (e^{-\epsilon/T})^{(n-m-2l)/2} \\ &= -mf + m\epsilon - T \frac{(n-m)}{2} \log(e^{-1/T} + e^{-\epsilon/T}) \\ &= -mf + m\epsilon + \epsilon \frac{(n-m)}{2} - T \frac{(n-m)}{2} \log(1 + e^{-(1-\epsilon)/T}). \end{aligned} \tag{6.4}$$

Differentiating with respect to m and setting the derivative equal to zero gives the following expression for the critical value of the force:

$$f_c = \frac{\epsilon}{2} + \frac{T}{2} \log(1 + e^{-(1-\epsilon)/T}). \tag{6.5}$$

When $T = 0$ we have $f_c(0, \epsilon) = \epsilon/2$. In addition, when $\epsilon < 1$, $\partial f_c / \partial T = 0$ at $T = 0$. When $1 \geq \epsilon > 1/2$ the behaviour at small T predicted by (6.5) is almost identical to that

derived from (4.2) (see figure 4). When $\epsilon \leq 1/2$ this strategy is no longer appropriate since the energy penalty incurred by having vertices in the β phase is larger than that incurred by having vertices leave the interface for the α phase.

The Motzkin path model differs in several ways. The walk can lie entirely in the interface at $T = 0$ so the ground state is unique even at $\epsilon = 1$. This means that the critical force has zero slope at $T = 0$, even when $\epsilon = 1$. In addition, $f_c(\epsilon, T) = \epsilon$ for the Motzkin path model.

For models with a degenerate ground state we would expect the force to have non-zero slope at $T = 0$.

In the physical situation when both solvents are poor the polymer could collapse (or precipitate) and this is not considered in our model since neither Dyck paths nor Motzkin paths exhibit a collapse transition. In principle this could be included by considering partially directed walks which are known to have a collapse transition (Brak *et al* 1992).

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